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STAT

RELATIONSHIP BETWEEN THE CONDITIONS OF CRYSTALLIZATION, STRUCTURE AND SHAPE OF CRYSTALS.

The inclusion of the outside medium into the structure of a crystal is a well-known fact, but its significance is not fully appreciated when evaluating the conditions under which the crystal is formed. Thus, for example, it is a popular opinion that the crystal lattice could be considered as fixed, while the shape of the crystal is regarded as something quite changeable. changes in crystal shape apparently result from very small changes in the crystal lattice. The nature of these changes could easily be attributed to a slight inclusion of the outside medium in the composition of the crystal.

The outside medium enters the crystal in the form of macro and micro inclusions and structural defects. A

The inclusions ~~could~~ be liquid, solid gaseous. When crystallizing under vacuum, vacuum inclusions could occur.

Structural defects are caused by incorrectly orientated elementary particles or larger complexes of particles of the crystalline substance; and by correctly and incorrectly oriented particles and complexes of particles of impurities, as well as inclusions of gas bubbles or groups of gas bubbles.

Defects and inclusions cause stresses and dislocations which change the relative velocities of growth of various faces. Inclusions which do not cause disruptions in the uniformity and the appearance of stresses may, when formed, reduce the velocities of growth of crystal faces.

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For any individual homogeneous type of crystal there is a characteristic final form. For example the crystal forms of sucrose and epsom salt ($MgSO_4 \cdot 7H_2O$) lead one to assume that for them this shape has a limiting simplicity. It consists of a minimum number of habitus faces which could enclose the volume. For pure sucrose crystals, this form is characterised by the following faces: 100 , 001 , 110 , and $1\bar{1}0$.

The majority of defects appearing during the growth of crystals from solutions are connected with the inclusion in the crystal of the solvent and of its impurities.

Apart from the composition of the growth medium, the conditions under which the crystallization occurs have a large influence on the structure of the crystal. These conditions are: supersaturation, temperature, and induced movement of crystal or solution. A detailed study of the process of inclusion of the growth medium into the composition of the crystal was made for sucrose crystals by one of the authors[4]

The quantity of solvent entering the crystal increases with increase in supersaturation. The last factor directly, but causes an increase in the difference in supersaturation on the crystal surface. Conditions are created for the covering of pockets of exhausted solution by the on-growing crystalline layer when there is a local deficiency of the substance necessary for crystal growth compared to the surrounding area; this pocket of depleted solvent is then left in the included corners of the growing layers. The differences

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in supersaturation increase, as well, with the increase in the size of the crystal.

H.E. Powers[2,3] observed similar phenomena from another point of view. He established a -fold increase in the water content of the sucrose crystal (from .01% to .4%) with increase in crystal size, explained the mechanism of formation of gaseous inclusions in sucrose crystals, and has clearly shown that the specific weight of sucrose crystals depends on the conditions of crystallization (due to variation in the amount of included material).

The increase in the percentage of water in sucrose crystals accompanying increase in crystal size, as established by Powers, is well explained by the fact that it is easier for supersaturation differences to occur on large crystal faces. This would lead to the inclusion of the mother liquor into the pyramids of growth of these faces. These phenomena were observed by one of the authors on mono crystals of epsom salt.

When growing these crystals by cooling the solution (the crystal holder was subjected to oscillating rotary movement), cases were frequently observed when crystal defects appeared, without any obvious reason, due to the formation in the crystal of the macro inclusions of the mother liquor; this was observed on the 4th/to 6th day when the supersaturation fell considerably but the temperature remained constant.

This could be explained apparently only by the fact that with increase in crystal size the local differences in supersaturation on crystal surfaces increased, increasing with it the probability of inclusion of mother liquor in places of

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"feed" deficiency.

Similar phenomena are observed for crystals of other substances. Apparently the formation of micro inclusions, which increases the percentage water content of crystals, goes on similar lines.

By increasing the velocities of rotation of the crystals, when growing epsom salt crystals, uniform crystals can be obtained at a supersaturation at which, previous to the increase in the speed of rotation, obvious inclusions of the mother liquor occurred.

Thus movement has an effect opposite to supersaturation and makes it more difficult for the outside medium to be included in the composition of the crystals. The more intensive is the relative movement of the medium and the crystal, the less are the differences in supersaturation on its surface and the more difficult it is for the outside medium to enter the crystal as an inclusion. Motion is opposite in its effects to supersaturation.

It must be mentioned that not all forms of relative movement between the medium and the crystal are equivalent. Rotation of the crystal removes the differences in supersaturation more effectively than a stirrer used for mixing. One-way rotation of the stirrer or of a crystal holder does not ensure a completely uniform "feeding" of the complex crystal surface. Such movement creates peculiar zones of stagnation and vortices, that is, it does not eliminate completely

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the non-uniformity of the solution, and hence does not effectively remove the differences in supersaturation on the crystal surface.

In connection with the above, a big advantage is attained by the reversible rotation of the crystal holder, the stirrer, or of a cylindrical crystalliser. This leads to a chaotic movement of the medium, ensuring the state of its maximum uniformity. It appears that the most chaotic movement is created by reversing rotation of the crystallizer.

In this form of motion, at the beginning, the crystallizer moves while the fluid remains stationary. Then, due to friction with the crystallizer walls, the liquid assumes rotary movement. When the crystallizer stops, the liquid continues to rotate.

Eventually the rotary movement of the crystallizer is reversed. The liquid, which still goes on rotating, is then subjected to the action of the walls, moving in an opposite direction, and from this moment the crystallizing medium is continuously in a state of chaotic motion. The particles move in extremely variable paths. To achieve the state of a chaotic movement, the change in the direction of rotation should be fast, not less than twice a minute.

The possibility of an effect of temperature on the outside shape of crystals has not been sufficiently studied, and is debatable. We have conducted several experiments to study this effect on the shape of epsom salt crystals.

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Crystals were rotated at initial temperatures of 25°, 30°, 33°, 35°, 37°, 40°, 43°, 45°, 48°, under conditions of strictly constant initial supersaturation, viz 1.2 gms. of heptahydrate salt per litre of solution, saturated at a given temperature.

At each temperature 2 to 6 uniform crystals weighing from 20 to 50 gms. were grown. The shape and size of seeding crystals, which were reduced when dissolving to "point" sizes, and the method of their attachment were the same for all experiments. Temperature, beginning from the 6th to 7th day of growth until the 20th day, was reduced by a total of 1°C for a litre crystallizer.

As the growth proceeded under conditions contributing to the attainment of uniform crystals, the initial shape of the crystal gradually became simpler and approached the practically uniform final shape characterised by the limiting simplicity corresponding to the shape of a homogeneous sucrose crystal

These shapes are formed by a prism 110 and a tetrahedron 111. Added to them are the extremely narrow faces of a pinacoid, and sometimes incipient 1 to 2 faces of a second tetrahedron.

The effect of the crystallization temperature on the final shape of a growing epsom crystal was manifest only in the increase in its length along "C" axis. At lower temperatures,

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narrow long crystals grow, at higher - more isometric. The slower the rate of growth of the crystal, the earlier and the quicker the reduction of the pinacoid faces occurs. It is difficult to obtain completely uniform crystals which have, at the same time, a shape of limiting simplicity. It is more difficult to obtain simple shape crystals at higher temperatures than at lower temperatures. Only such crystal was obtained at 48°C.

Because the change in the crystallization temperature of a solution at the same supersaturation is frequently accompanied by a significant change in its concentration (for $MgSO_4 \cdot 7H_2O$ it is very high), it is difficult to isolate the sole effect of temperature. The observed variation of the shape could as well be attributed to the changes in the concentration.

Apart from the above, for ionic solutions we have to take into consideration a considerable change in the structure of solutions with a change in the temperature of crystallization. The structure of highly concentrated solutions approaches that of the crystallizing salt. This facilitates orderly inclusion of the solvent into the crystallizing lattice of the homogeneous crystal. Since at different concentrations the liquid medium is different, this creates changes in the character of its relationship with the crystal, it may be expected that its inclusion in the crystal composition will be different.

The above principle outlining the influence of the medium on its inclusion in the crystal content does not exclude the presence of the surface effects of the medium, but apparently the most efficient mechanism of surface effects is the ex-

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that leads to the inclusion of the medium in the composition of the crystal. This can be explained by the following example[1].

While the octahedron faces of potash alum crystals cannot be dyed by Ind. 918, the cube faces can. This means that when growing from a solution containing the dye, the octahedron faces must repel this impurity; thus they must perform additional work. Consequently, the velocity of their growth should be slowed down. Contrary to the above, the cube faces which include or absorb the impurity should not experience retarding of growth. Thus the octahedron faces should have increased in size whereas the cube faces should have been "wedged out". In fact, the opposite of the above occurs. The cube faces absorbing the impurity increase in size and the transparent octahedron faces are "wedged out".

The mechanics of the slowing down of the growth of the cube faces is apparently connected with the blocking of the dye particles of the edge elements of the contours of this face, that is, the edges of the steps formed by the tangentially spreading layers of the growing "edges of the helical turns". But such blocking leads to the inclusion of the impurity into the crystal composition, which is shown by the colouring of the pyramids of growth of the cube faces.

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Thus out of the ways of surface influence of the medium on the crystal, the more effective way which determined the change of shape was proved to be the way connected with the inclusion of the impurity in the crystal content. The final shape of homogeneous sucrose crystals must differ from the equilibrium shape by the simplicity of the combination of its faces. The crystal of the final shape does not have the important secondary faces, which blunt the corners and the edges.

With respect to the relative magnitude of the face areas, the crystal shape which is nearest to the equilibrium shape will be apprently a "final shape" intrinsic to a crystal having stoichiometrice composition and a maximum physical uniformity.

For sucrose, we can anticipate that such crystals could be obtained at higher temperatures under conditions when the decomposition of solution during the period of crystal growth is still so small that its influence can be ible.

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REFERENCES

1. [illegible]-Malkov, V. Y. 1959. Concerning the Question of Crystal Growth in the Systems Containing Impurities, published in Volume 4, No. 1, Crystalography.

2. Powers, H. E. S. 1956. Growth of Sucrose Crystals. Nature 178:139.

3. Powers, H. E. C. 1956. Sucrose Crystal Studies. Intern. Sugar Journ., 58:246.

4. Shefal, I. N. 1956. Real Crystal Formation: Growth of Crystals. Reports at the First Conference on Crystal Growth. Moscow pp.1-34. English Translation Consult Bureau Inc.

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CRYSTALLIZATION VELOCITY OF SUCROSE AT HIGHER TEMPERATURES

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Crystallisation is the main process in the sugar industry since the operations preceding

only the preparatory phases of producing crystallised sugar.

The maximum production of a finished product i.e. white granulated sugar of high quality. or raw sugar, as well as the utmost exhaustion of ~~intercrystallisation~~ the syrup depend upon a

The process of sugar crystallisation is very complex and depends on many factors, such as the coefficient of supersaturation, purity, temperature etc., which influence crystal growth velocity.

One of the most important factors in practice is the temperature of crystallisation.

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of sucrose

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develop a method of obtaining pure properly faceted crystals of sucrose in great quantities and design an apparatus that would help to avoid crystallizing the supersaturated solution.

1. To obtain good crystals for testing the following method was developed:

Some 1 l. of pure sugar solution containing 72-73% of sucrose is placed into a wide-necked 1 l. capacity conical flask which is open at room temperature for generating crystals. After 5-6 days the crystals, properly faceted and weighing less than 0,1 gm., were separated from the solution by means of a wooden spatula, washed with absolute alcohol and stored in a closed glass vessel. The increase in weight of crystals up to 0,4-0,8 gm. required for tests, was made during 10-14 days at room temperature.

More concentrated sugar solutions are not suitable since they may on the surface and are easily crystallized. Each crystal was suspended in the flask with a silk thread which was cut when the crystal reached a definite weight. For the final growth of crystals wire with sharp edges was used and

and immersed in solution of the same concentration for 10-12 hours. After this period the crystal was taken out, washed with absolute alcohol, wrapped in oil paper and kept in a desicator.

This method results in a great number of crystals faceted like plate glass and

2. For evaluating sucrose crystallization velocity at high temperatures the following unit was developed.

The apparatus consists of main parts: crystallizer receiver and viscosimeter

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The Crystallizer is a glass flask with round bottom and necks. The openings of the flask are closed by ground stoppers and with a vacuum grease. To the right side of the crystallizer tube with a -inlet glass stop-cock was joined. One of the cock tubes was connected with a water vacuum pump by means of a rubber tube. The second opening of the cock served for connecting it with a flask receiver. The -inlet cock protruded above the water surface of a thermostat, thus allowing it to be turned in any direction.

30 cm. 20 mm.

The holes of the tubes were closed with ground conical polished stoppers having 5 6 mm. openings in the end. A glass tube with an electric spiral wrapped in asbestos was put on the cone. The spiral heaters of the stoppers were connected with each other successively and switched on. A 40-42 mm long quarts thread was inserted into each tube to support a

preweighed on an analytical balance. The quarts thread was fastened to the conical part of the stopper by means of a supporter . The upper parts of the stoppers were closed with cotton wool wadding to avoid the moisture of the air. Then the glass tubes containing the crystals were placed in the thermostat.

A supersaturated solution of sucrose was transferred

1 l. capacity flask with polished stoppers.

Into of the flask openings a thermometer was inserted, and through another the flask was connected with the crystallizer and viscosimeter by means of -inlet cock. The middle opening was used for pouring the solution.

The viscosimeter consists of glass tubes connected with each other tube 1 has an extension (where small lines a and b are drawn), and The capacity of the wide

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part was 5 ml. tube 1 was connected with the
The supersaturated solution was drawn in when a vacuum was created in the viscosimeter. The necessary volume of the solution in the viscosimeter was made up to the mark on tube bulb 2 with a pipette. Calibration of the viscosimeter was made at 67.1% of sucrose solutions at 20°. The elastic 35 - 40 cm. long balance quarts thread placed on the steel wire with collars was well fastened on the microscope support ( ). The quarts thread might be lowered or raised of microscrews, the sucrose crystal thus being

sugar solution

consisted of the microscope support, the microscrew and a stand on which the microscope tube with object-lens and eye-glass of triple magnification was horizontally fixed. For placing the balance quarts thread in 0 position and measuring the magnitude of its deflection due to the increase of the crystal weight, cross-shaped lines were drawn in the eye-glass. During testing the balance quarts thread was placed under the glass cover to protect it from air currents.

The thermostat, a rectangular 80 l. capacity glass vessel, was filled with water and nichrome spirals were used as electric heaters. They were placed in a brass jacket to protect them from corrosion. A contact thermometer was used with the 1200 watt capacity heater. Water temperature of the thermostat was measured with a 100° thermometer to within 0.1°.

Before placing the crystalliser into the thermostat
were closed with ground polished stoppers and it was fastened to the support in an exactly vertical position. The receiver was connected with the crystalliser by means of the glass tube with the -inlet cock. To measure the temperature of the sugar solution a thermometer was put into it. The viscosimeter was also connected with the receiver. The whole system was so arranged that by opening the inlet cocks K and 1 (Figure 1) the supersaturated sugar solution from the receiver into the viscosimeter and crystalliser

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by means of a vacuum.

The whole system of the apparatus was fixed on supports connected with each other and placed into the glass thermostat. The thermostat was heated up to the test temperature, then of the heaters switched out, the second being switched on through the rheostat. To keep the thermostat water temperature constant (i.e. in the crystallizer and the viscosimeter), a thermoregulator with a contact thermometer was used.

The crystals of sucrose in glass tubes were also placed into the thermostat (Fig. 3) to reach the testing temperature. When the apparatus was quite ready the receiver was filled with the supersaturated solution To obtain evaporated in the water bath and a calculated amount of water removed. The percent of dry substances in the solution was determined by means of polarimeter and refractometer.

When the supersaturated solution of sucrose in the receiver reached the testing temperature it was drawn into the crystallizer and viscosimeter, and taken into a pycnometer by means of a pipette provided with a cock.

Then the sucrose crystal suspended on the quarts thread and heated in the tube was raised into the conical part of the apparatus, transferred into the crystallizer, suspended from the quarts balance, closed with a glass cover and 0 position of the balance quarts thread was observed by the cathetometer. After the period of crystal weight increase was over, the extent of the balance quarts thread deflection was measured and the crystal weight increase estimated. The process was repeated for each crystal tested.

3, In using the above apparatus a method was developed which allowed making a direct measurement of the crystal weight increase in the solution by means of elastic quarts thread

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the equation deduced for determining an absolute increase of crystal weight

where:

n - a number of divisions according to the cathetometer.

a - a value of scale division in mg.

d_c - a specific gravity of sucrose in gr/cm^3.

d_p - " " " " the solution in gr/cm^3.

An estimate of the crystal weight increase was made by means of the cathetometer through measuring the quartz thread deflection from its 0 position after the period of the crystal growth was over. The scale had been previously calibrated. The comparative tests in evaluating the sucrose crystallization velocity at 30° by the direct weighing method and by the elastic quartz thread agreed with Prof. I.A. Kuhka-renko's data.

4. A comparison of methods with sucrose crystallization in pure sugar solution at 75° without stirring showed the advantage of the second method, as can be seen from Table 1.

Table 1.

Supersaturation coefficient K	Crystallization velocity in mg/m^2 min. By the method of elastic quarts thread.	By the weighing method.
1,044	1112	1063
1,056	1737	1700
1,069	1923	1914
1,115	3380	3251
1,162	4526	4127

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The difference between these methods was 0.55 - 4.7% and was caused by wiping and washing taken out of the solution in the weighing method. There might also be some losses of sugar. The disadvantage of this method consists in to outside disturbances that should be taken into account during an experiment[3,4]

5. The sucrose crystallization velocity in pure sugar solutions was determined at 70°, 80°, 90°. The data obtained are given in Table

Table 2.

Sucrose crystallization velocity in pure sugar solutions at 70°, 80°, 90°.

Temperature °C	Sugar content %	The coefficient of supersaturation of the solution K.	Sucrose crystallization velocity in mg/m² min.
70	76.7	1,009	287
	77.5	1,057	1441
	78.0	1,090	2213
	78.3	1,103	2537
	78.8	1,135	3272
	79.2	1,169	3814
80	79.2	1,034	1000
	79.9	1,078	2446
	80.4	1,111	3368
	80.8	1,139	4151
	80.0	1,151	4632
	81.4	1,183	4951
90	81.2	1,023	946
	81.5	1,040	1662
	81.9	1,065	2704
	82.0	1,079	3026
	82.3	1,102	3830

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Fig. 8 shows that the crystallization velocity is in a direct relationship to the excess supersaturation and is expressed as a straight line. The increase of the sucrose crystallization velocity in pure sugar solutions within the range of 70-80° per 10° is expressed 1.25 times, and within 80-90° as 1.3 times. It is interesting to note that the viscosity of the saturated sugar solutions has a minimum value at 70° as is seen from Table 3.

Table 3.

Temperature	20	30	40	50	60	70	80	90
Viscosity in poises	224	163	126	102	90	82	85	92

It has, therefore, been previously supposed that the crystallization velocity at 80 and 90° is less than at 70°. however from our tests velocity was increased. It is then apparent. that viscosity does not play the part some investigators suggested it does, and this has been pointed Van Hook.

6. The velocity of crystallization of sugar syrup with a purity of 93,08 at 70°, 80°, 90° was determined under the above conditions. The results obtained are given in Table 4 and 5.

Table 4

Sucrose crystallization velocity in sugar syrup with purity of 93.09 at 70°, 80°, 90°.

Content of dry substance %	supersaturation coefficient.	Sucrose crystallization velocity in mg/cm² min. Crystal Numbers.				Temperature of the solution.
		1	2	3	Average	
78.3	1,027	449	427	434	437	
79.0	1,071	958	1031	1088	1026	
80.0	1,138	1590	1674	1698	1654	70°
81.0	1,221	2403	2549	2436	2433	

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82.3	1,323	3238	3186	3284	3236	
80.4	1,031	652	669	675	665	
81.3	1,093	1464	1460	1516	1480	
82.0	1,145	2164	2171	2064	2133	80°
83.1	1,236	3153	3126	3069	3116	
83.9	1,310	3662	3586	3474	3574	
82.2	1,018	675	748	791	738	
82.3	1,025	833	946	927	902	
83.1	1,084	2073	2134	2107	2105	90°
83.6	1,124	2573	2479	2538	2530	
84.1	1,166	3005	2989	3020	3005	

Table 5.

The dependence of sucrose crystallization velocity on the supersaturation coefficient in sugar syrup.

coefficient of supersaturation	Sucrose crystallization velocity in mg/m² min. at the temperatures :		
	70°	80°	90°
1,025	437	560	902
1,050	775	950	1375
1,075	1075	1325	1800
1,100	1350	1650	2175
1,125	1575	1950	2550
1,150	1825	2250	2850

The results are also graphically depicted in

The conclusions

zation in pure sugar solutions, since in both cases the purity does not greatly differ. The situation becomes different at lower purity.

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Up to now the optimal temperature of boiling last massecuites has not been found. Boiling is made at higher as well as at lower temperatures. Therefore, it was necessary to solve this problem.

For making tests a low raw with the purity 79.28% was taken. grade often met with at sugar factories. A determination of the crystallization velocity was made at temperatures 70, 80 and 90°. The data obtained are given in Tables 6 and 7 and graphically shown

Table 6.

Content of dry substances %	Sugar content %	Non-sugar water ratio	apparent coefficient of supersaturation	Crystallization velocity in mg/m² min. Crystals 1	2	3	Average
At the temperature 70°C							
81.3	64.46	0.901	0.054	70	66	62	66
81.5	64.61	0.913	1.068	90	92	84	89
82.0	65.01	0.944	1.104	144	147	131	142
82.5	65.41	0.977	1.142	191	162	170	174
84.1	66.64	1.093	1.278	313	307	327	316
84.79	67.13	1.145	1.340	339	320	349	336
At the temperature 80°C							
83.0	65.80	1.012	1.045	57	56	63	59
83.5	66.20	1.049	1.083	132	120	115	122
84.0	66.59	1.088	1.124	187	217	185	196
84.5	66.99	1.130	1.167	244	302	2356	260
85.0	67.38	1.174	1.213	279	320	304	301
At the temperature 90°C							
85.0	67.38	1.174	1.064	-	45	33	39
85.7	67.94	1.242	1.126	140	97	108	115
86.5	68.57	1.328	1.201	244	197	232	224
87.0	68.97	1.387	1.257	284	285	236	268
87.6	69.45	1.462	1.327	342	393	366	367

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Table 7.

supersaturation coefficient	sucrose crystallization velocity in low raw in mg/m² min. at the temperatures:		
	70°C	80°C	90°C
1,025	45	75	60
1,050	85	133	110
1,075	120	180	150
1,100	153	218	187
1,125	183	258	223
1,150	215	293	255

The above figures show that the sucrose crystallization velocity in low raw increases with the coefficient of supersaturation only up to 80°. With the increase of temperature and supersaturation coefficient the crystallization velocity decreases, as was shown for 90°.

This phenomenon should be accounted for by the increase of the non-sugar water ratio which greatly increases at 90°. It then follows that the optimal temperature of last massecuites boiling lies within 75 80°. With last massecuites boiling under beet-sugar factory conditions, and possibly at cane sugar factories too, I should like to draw attention to the following facts:

The Last massecuites are usually boiled up to a high concentration, 96%. After it has been transferred into the crystallizer, it is usually given water in the process of crystallization to concentration accepted as 92% in centrifugal work. Taking, however, into consideration the tests that have been carried out, as well as some work at several factories, this method is considered wrong for the following reasons: When a massecuite is boiled up to 96% of dry substances its viscosity greatly increases and it becomes more immobile. Therefore heat transfer becomes worse and at the heating surface the crystal mass is overheated 20° and more depending on the temperature of the heating vapour. This results in sugar decomposition. Moreover, some non-sugars are evidently decomposed, thus making

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the work of centrifugal machines worse.

It is known that some non-sugars at higher concentration are positive molasses formers, whereas at lower concentrations they are negative molasses formers. This can be said of the decomposition products of pectin substances, e.g. araban at a concentration lower than 0.1% is a negative molasse-former and raises the crystallization velocity, but at a concentration of over 0.1% becomes a positive molasse-former and decreases the crystallization velocity. Such is the behaviour of some other non-sugars - raffinose, calcium acetate etc. Therefore, when massecuites are boiled up to 96% of dry substances, the quantity of water in the massecuites is 4% and the concentration of non-sugars is high. In this case they increase sucrose solubility and promote molasses formation. If massecuites are boiled up to 92% of dry substances, then the water content is 8%. In this case non-sugars have a lower concentration, decrease sucrose solubility, improve sugar crystallization in a vacuum-apparatus and decrease molasses formation.

A favourable influence on sugar crystallization goes on in the crystallizers from the moment massecuites have been dropped. This has been confirmed by some experiments made under factory conditions. Boiling time and quantity of vapour are reduced. The final result of crystallization in a vacuum-apparatus and in the crystallizers reaches sometimes 22 24 units instead of usual 16 18 under the conditions of beet sugar factory. Therefore, the above suggestion reads as follows:

"To boil massecuites up to the concentration it ha when transferred centrifugal machine, the massecuites should be cooled 5 10° lower than the temperature in the centrifugal machine work. Then it must be heated up to the temperature which is accepted in centrifugal machine work at a sugar factory".

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LITERATURE

1. Gerasimenko, A. A., Bolovin, P. V., Abramova, M. A. [illegible]. Sakh. Prom. N 11:71.

2. Gerasimenko, A. A., and Bolovin, P. V. 1956. The works of the Kiev Technological Institute of Food Industry named after A. I. Mikoyan. B-14:158.

3. Gerasimenko, A. A., and Bolovin, P. V. 1955. The Ukrainian Chemical Journal, XXI, B-1:527.

4. Gerasimenko, A. A., and Bolovin, P. V. 1955. The Ukrainian Chemical Journal XXI, B-4:792.

5. Gerasimenko, A. A., and Bolovin, P. V. 1956. The Ukrainian Chemical Journal XXI, B-5:[illegible].

6. Gerasimenko, A. A., and Bolovin, P. V. 1956. The works of Kiev Technological Institute of Food Industry named after A. I. Mikoyan. B-11:[illegible].

7. Bolovin, P. V., Gerasimenko, A. A., and Abramova, M. A. 1956. Sakh. Prom. N 3:10.

8. Bolovin, P. V., and Gerasimenko, A. A. 1953. The works of Ukrainian Institute of Sugar Industry, B-11:124.

Approved For Release 2009/04/15 : CIA-RDP80T00246A006800190002-5

Approved For Release 2009/04/15 : CIA-RDP80T00246A006800190002-5

LITERATURE

1. A.A. Gerasimenko, P.V. Golovin, M.A. Abramova.
Sakh. Prom. N 11, 71 (1957).

2. A.A. Gerasimenko and P.V. Golovin.
The works of the Kiev Technological Institute of Food Industry named after A.I. Mikojan: B-14, 156 (1954).

3. A.A. Gerasimenko and P.V. Golovin.
The Ukrainian Chemical Journal, XXI, B-13, 527 (1955).

4. A.A. Gerasimenko and P.V. Golovin.
The Ukrainian Chemical Journal, XXI, B-6, 792 (1955).

5. A.A. Gerasimenko and P.V. Golovin.
The Ukrainian Chemical Journal, XXI, B-6, 797 (1955).

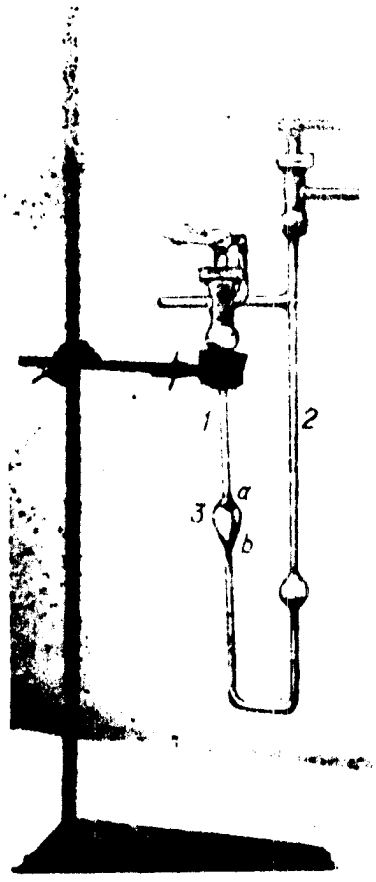
6. A.A. Gerasimenko and P.V. Golovin.
The works of Kiev Technological Institute of Food Industry named after A.I. Mikojan. B-16, 17 (1956).

7. P.V. Golovin, A.A. Gerasimendo and M.A. Abramova.
Sakh. Prom. N 3. 10 (1958).

8. Prof. P.V. Golovin, the post graduate A.A. Gerasimenko.
The works of Central Institute of Sugar Industry, B-11, 124, (1953).

Approved For Release 2009/04/15 : CIA-RDP80T00246A006800190002-5

Approved For Release 2009/04/15 : CIA-RDP80T00246A006800190002-5



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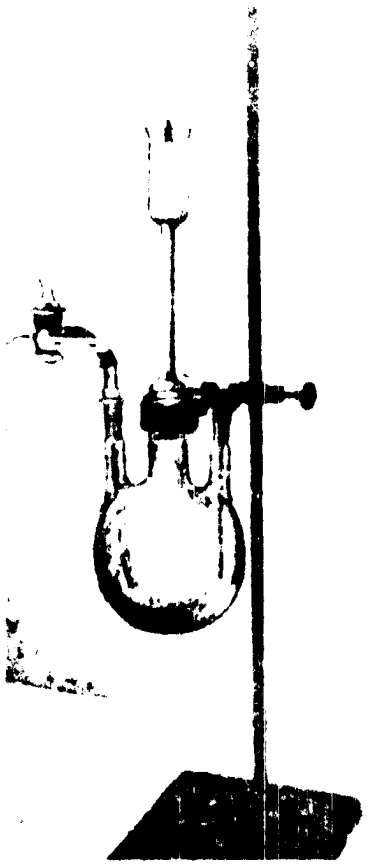

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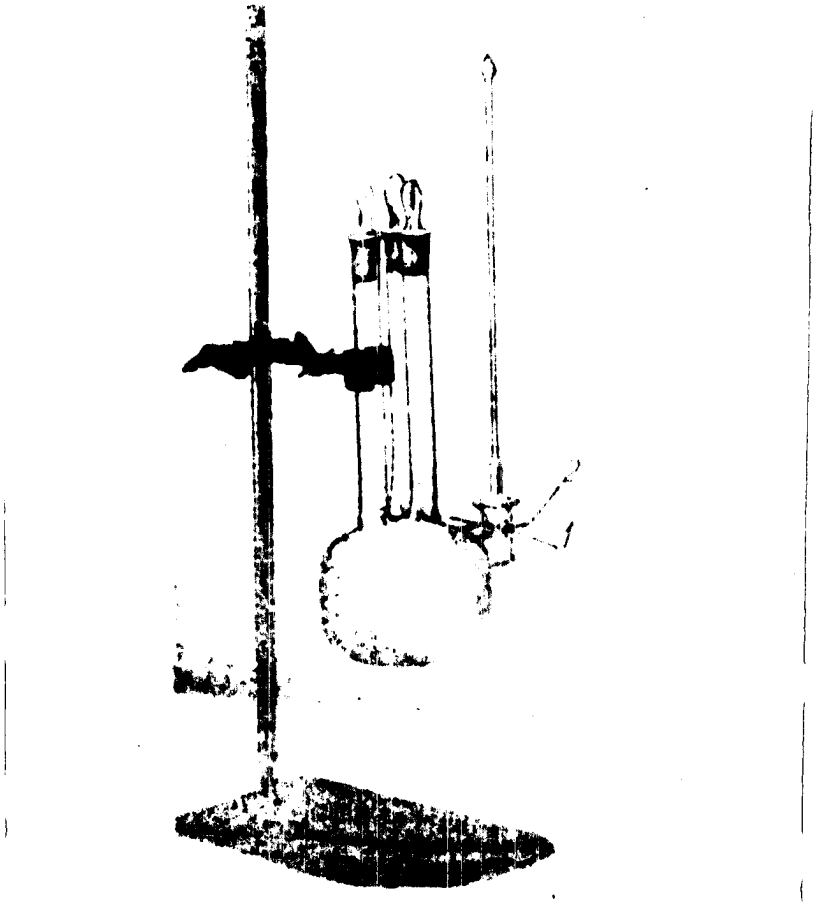

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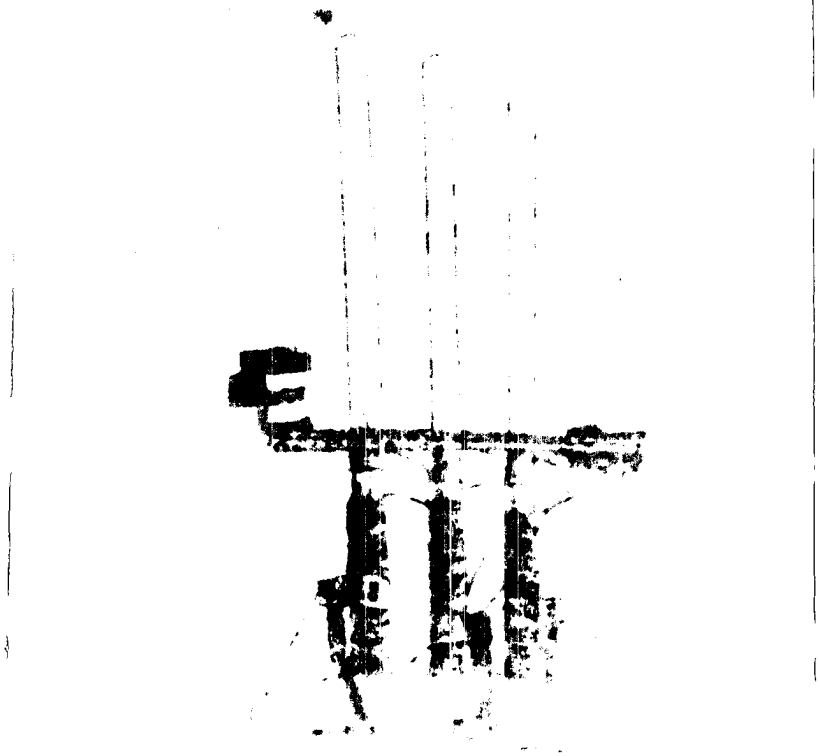

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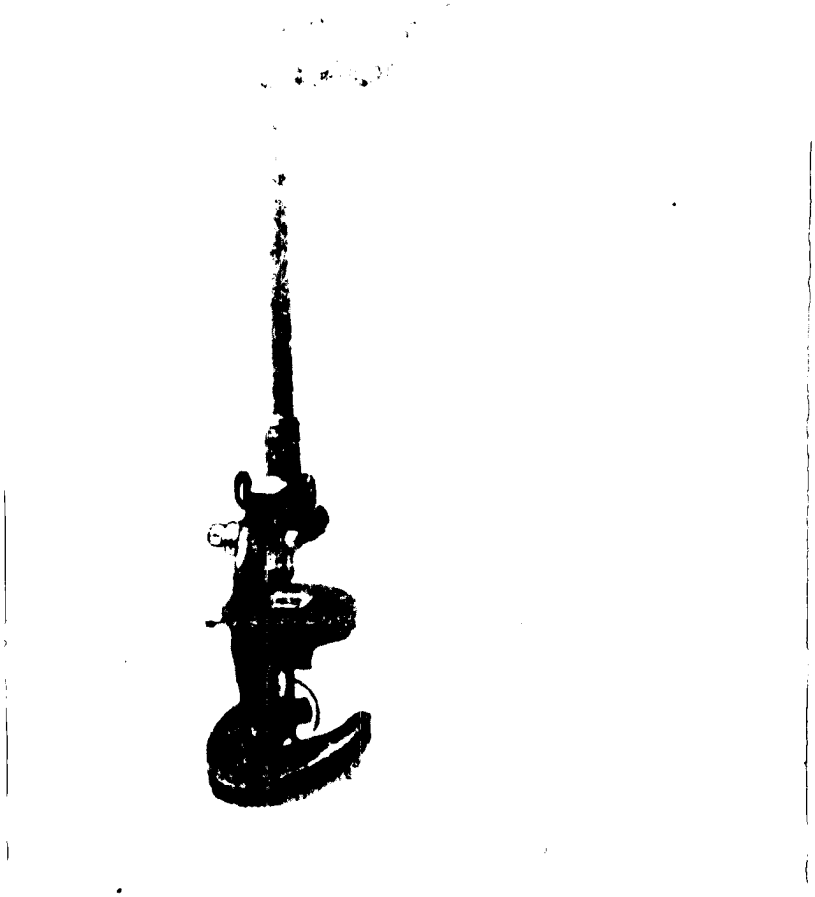

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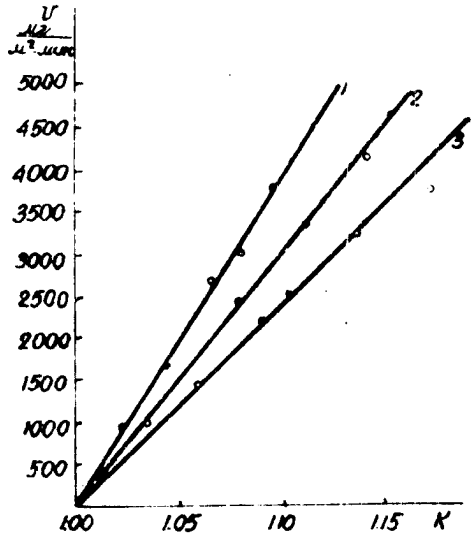
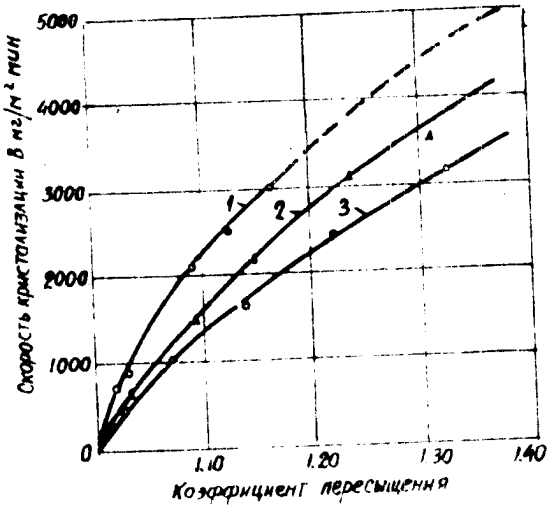


Зависимость скорости кристаллизации сахарозы (V) в чистых сахарных растворах от коэффициента пересыщения (K). 1 — при 90°; 2 — при 80°; 3 — при 70°.

Рис. 8



Зависимость скорости кристаллизации сахарозы в сахарном сиропе от коэффициента пересыщения.
1 — при температуре 90°; 2 — 80°; 3 — 70°

Рис. 9

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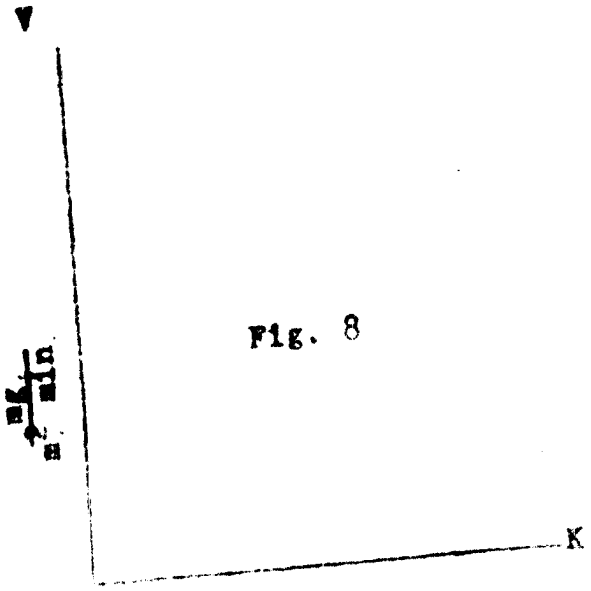

Fig. 8

Relationship between the velocity of crystallisation of sucrose (V) and coefficient of supersaturation (K), in solutions of pure sucrose.

1 - at 90°; 2- at 80°; 3-at 70°.

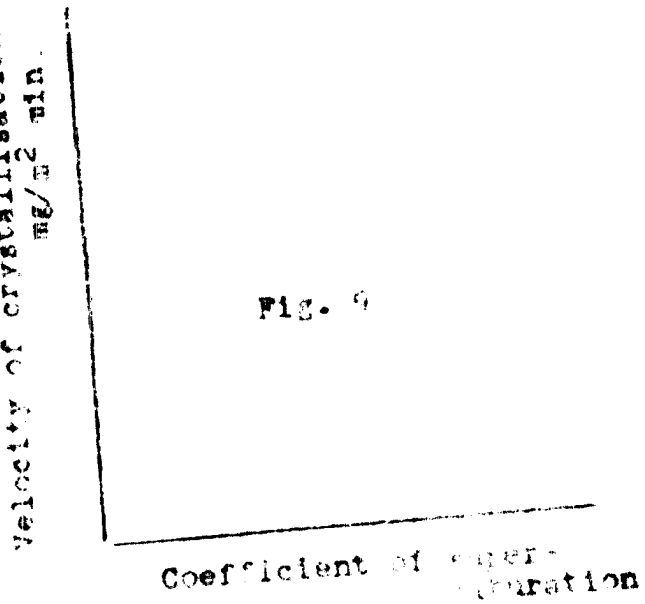

Fig. 9

Relationship between the velocity of crystallisation of sucrose and coefficient of supersaturation in (sugar) syrup.

1 at the temp 90°; 2 - 80°; 3 - 70°.

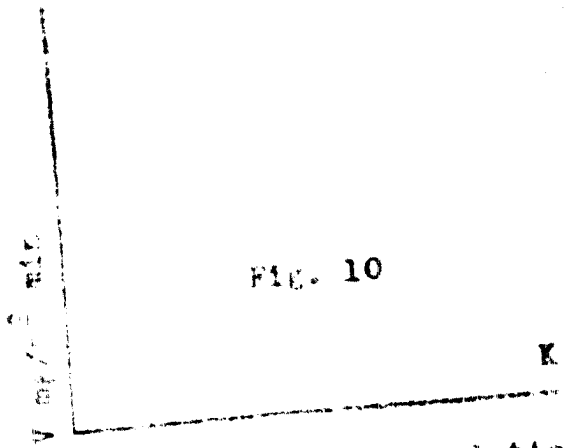

Fig. 10

Graph showing the relationship between the velocity of crystallisation and excess supersaturation.

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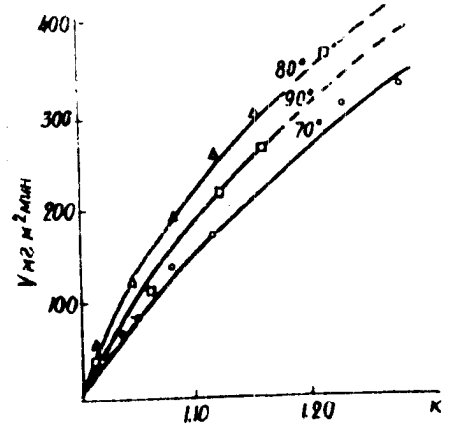

График зависимости между скоростью кристаллизации и избыточным пересыщением

Рис. 10

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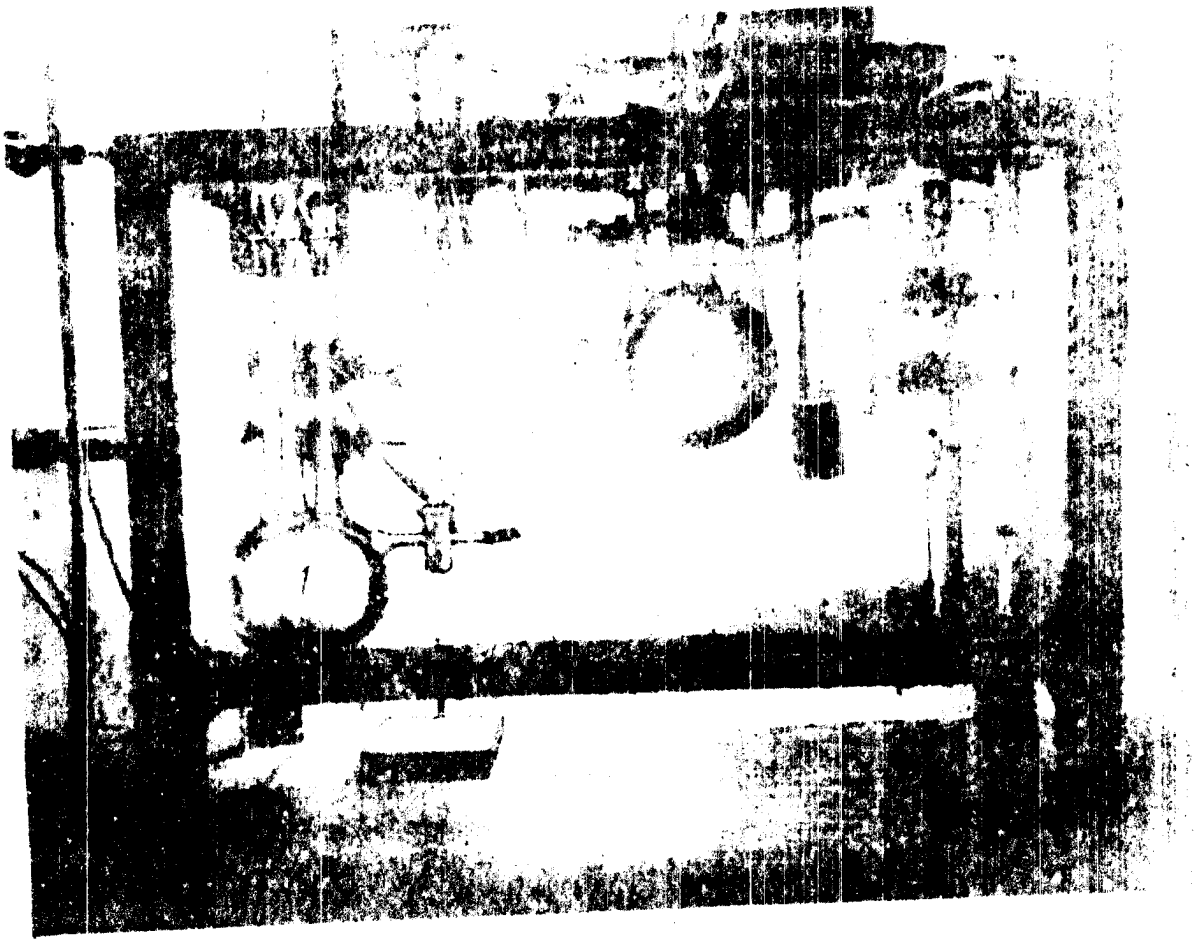

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STAT

The coefficient of supersaturation is determined in pure and impure sugar solutions. Several methods have been proposed for such determination, there being, however, no uniform method up to now.

Evaluation of the supersaturation coefficient in pure sugar solutions.

The following equation is used for determining the supersaturation coefficient in pure sugar solutions.

$$\psi = \frac{S}{\sigma} \qquad /1/$$

where ψ - the coefficient of supersaturation;

S - sugar content in water unit of the solution dealt with; in %;

σ - sucrose solubility in water unit in the state of saturation at the same temperature /taken from a table, e.g., from Herzfeld's/.

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Example 1. A supersaturated sugar solution at [illegible] contains 68,154 gr. of sucrose to the weight of the solution. Water content in the solution is 31,846. Sucrose content in 1 gr. of water is 2,108 gr. Sucrose content in the saturated sugar solution in water unit at 20° according to Herzfeld is equal to 2,039. Then,

$$\psi = \frac{2,108}{2,039} = 1,034.$$

There is a method of evaluating a degree of the supersaturation of the sugar solution which is measured by an excess of the [illegible] sugar in 100 cm^3 of the saturated solution at the same temperature.

The determination of the degree of the supersaturation is made by the formula:

$$\Delta = Z_1 \gamma_1 - Z_2 \gamma_2 \qquad /2/$$

where Δ is the degree of the supersaturation in gr/100cm^3;

Z_1 - sugar content in 100 gr. of the solution taken for an investigation;

Z_2 - the same in 100 gr. of the saturated solution;

γ_1 - a specific gravity of the investigated solution

γ_2 - a specific gravity of the saturated solution.

Example 2. We have in Example 1 $Z_1 = 68,154$, $\gamma_1 = 1,[illegible]$, $Z_2 = 67,09$, $\gamma_2 = 1,334058$. Substituting these values we obtains $\Delta = 91,03 - 89,51 = 1,52$ gr/100cm^3. Before we deal with the method of determining the coefficient of supersaturation in impure sugar solutions, let us define a physical

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value of the supersaturation coefficient. To fulfil it we should consider Kossel's theory of crystallization. According to this theory energy in homeopolar crystals is defined as the potential energy of the interaction between the two nearest individual particles with distance. It ca. therefore, be admitted that the value of the supersaturated coefficient is to show how of sucrose molecules has been increased in water unit and the distance between them decreased to such an extent that the power of interaction between them becomes sufficient to overcome an average resistance and to create a crystal lattice or to [illegible] particles on the facets of the finished crystal [illegible] This supposition, however can only be made without taking into consideration the influence of other factors participating in the process of crystallization, such as: adsorption layer, hydration of sucrose molecules, hydrogen dipoles of nonsugars, viscosity etc. To demonstrate the above suggestion, we may point out that in Example 1 the distance between molecules in the state of saturation is 10,83Å, for supersaturation - 10,19Å. Thus, the coefficient of supersaturation ψ = 1,034 and the degree of supersaturation = 1,52 gr. showed such a binding of molecules which in introducing the crystallization centers creates the crystallization of sucrose.

Hc

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determination of the supersaturation coefficient in impure sugar solutions.

The determination of the supersaturation coefficient in impure sugar solutions can be made as well as for pure sugar solution according to the formula: /1/.

The green sirup has the following content;

TDS = 87,0; TP = 76,6; S = 66,12; t = 80°;

σ = 3,82. Then:

$$\psi_1 = \frac{66,12}{13,6 + 3,82} = 1,4$$

Where:

TDS - True dry substances determined by weight;

TP - True purity;

S - Sugar;

σ - Solubility of sucrose according to the table by Herzfeld for 80°;

ψ_1 - coefficient of supersaturation.

This supersaturation coefficient corresponds to the moment of crystal forming from the green sirup with the above content. These higher values of the supersaturation coefficient in massecuittes of lower purity are explained by the presence of nonsugars. It then follows that the physical effect of nonsugars consists in their arranging themselves between the molecules of sucrose thus increasing the distance between them. As a result, the power of mutual interaction and the crystallization velocity are decreased. Besides,

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a presence of nonsugars shows a resistance towards a mutual interaction of the molecules.

In the above Example ψ_1 being 1.4 , the distance between molecules is 10,24Å. Since the investigation showed that in impure sugar solutions the solubility of sucrose varies ,being higher or lower than that in pure solutions at the same temperature, depending on purity, several formulas have been developed for defining the supersaturation coefficients in impure sugar solutions. These formulas are intended to consider an influence of nonsugars upon the crystallisation velocity of sucrose. The following formula has been widely used:

$$\psi_2 = \frac{\text{Sucrose/water in saturated solution at the same temperature and purity.}}{\text{Sucrose/water in}} = \frac{S}{s} \qquad /3/$$

It is necessary to point out that in order to determine the supersaturation coefficient according to this formula the solubility of sucrose in impure sugars solutions should be defined. It should be made for each investigation, since raw materials differ in quality depending upon various regions growing conditions, fertilizers used and storing. Therefore , sugar solutions also differ in their capacity to dissolve sucrose. There have been some attempts to develop tables of sucrose solubility in impure sugar solutions for various purities and temperatures, for example, Fradisz's, Honig and Spencer's tables. But their values for the strups of the same purity and temperatures differ greatly as in Table 1.

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Table 1

Sucrose solubility in impure sugar solutions according to

Syrup purity	Fradisz	Hoeglund	Grut
81,0	3,34	3,992	3,920
72,0	3,75	3,446	3,40
66,7	4,05	4,128	3,91
60,0	4,24	4,794	4,57

Table 1 shows several figures of sucrose solubility in impure sugar solutions at 70°. The values differ greatly especially with a decrease of purity, the difference amounts to 0,22 - 0,3 - 0,54. It is, therefore, necessary to determine the solubility of sucrose in impure sugar solutions for each evaluation of the coefficient of supersaturation. It is, of course, possible to develop tables for various regions, showing some average data of sucrose solubility in impure sugar solutions. There is, however, no certainty as to an accuracy of these values. Meanwhile an solution of any problem supposes one-answer solution. It is, therefore, necessary to have an original basis constant. In the meantime, the solubility of sucrose in impure sugar solutions is not a value definitely fixed at the given purity and temperature and varies within a considerable range. That is why there were several formulas developed for defining the supersaturation coefficients in im-

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ure sugar solutions. Let us now determine the supersaturatio coefficients by means of these formulas and compare their values. For comparison we take the green syrup with the content shown in Example 3. For [redacted] this the sucrose solubility, according to Brut, is 4,02 at the temperature indicated. Then, according to the formula /3/, we find:

$$\psi_2 = \frac{[redacted]}{4,02} = 1,[redacted]$$

The two following formulas given by McGinnis have been modified by us and run as follows:

$$\psi_3 = [redacted] \quad /4/$$

$$\psi_4 = \frac{S}{\frac{S}{1} \cdot S_1 \cdot W} \Big/ \frac{S_1}{\frac{1}{1} \cdot S_1 \cdot W} \quad /5/$$

where - S - the quantity of sucrose in water unit of the solution used, in gr.

S_1 - the sucrose solubility in water unit of the saturated solution at the same temperature and W in gr.

W - the quantity of impurities in water unit of the solution used.

For this example we have:

S = [redacted]; S_1 = 4,02 and W = 2,406. Water value = 1

By substituting these values we find:

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$$\psi_3 = \frac{\dfrac{5{,}08 + 3{,}606}{1 + 5{,}08 + 1{,}606}}{\dfrac{4{,}08 \quad 1{,}606}{1 + 4{,}08 + 1{,}606}} = \frac{0{,}87}{0{,}8461} \quad 1{,}025$$

$$\psi_4 = \frac{\dfrac{5{,}08}{1 + 5{,}08 + 1{,}606}}{\dfrac{4{,}08}{1 + 4{,}08 + 1{,}606}} = \frac{0{,}6618}{0{,}6606} = 1{,}0$$

The formula [illegible] suggested by [illegible] is as follows:

$$\psi_5 = \frac{\quad}{[1 + a_1 (\quad)] \times (0{,}96 + 0{,}39\ \quad)} \quad N$$

where [illegible]

t_{sr} the solution boiling temperature[illegible]°,

t_v - water boiling temperature at the same pressure.

For example taken the temperature difference in

$t_{sr} - t_v$ [illegible] 90° - 82,3 = 17,7

$\lg 9 = \lg 76 + 1{,}[illegible]$;

[illegible]

$$\psi_5 = \frac{\quad}{[1 + a_1 (\quad)] \times (0{,}96 + 1{,}3)}$$

$$\psi_5 = \frac{\quad}{[illegible] \times 1{,}26} \quad 1{,}03$$

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Comparing the supersaturation coefficients obtained we find:

$\psi_1 = 1,40$

$\psi_2 = 1,2$

$\psi_3 = 1,0$

$\psi_4 = 1,05$

$\psi_5 = 1,63$

Evidently, such results cannot be recognized as satisfactory, since it is necessary to take into consideration that in the solutions of high purity the saturation at the crystal forming amounts to 1,2 and after the crystal formation and at the crystal growing it is 1,1. Then it appears that the coefficients of supersaturation at the lower purity are lower than those in the solution of higher purity and that is impossible. That is why [illegible]

Considering the process of crystallization from the standpoint of chemical thermodynamics, M.G.Kaveem[5] indicated that the existing methods of defining the supersaturation coefficients are not theoretically founded and suggested using theoretical coefficients of supersaturation which are expressed as a ratio:

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$$\text{Solution activity} \quad \text{or} \quad \text{Sugar activity in solution}$$
$$\text{Crystal activity} \qquad \text{Crystal activity}$$

It is, however, necessary for practical purposes to accumulate sufficient material for determining these activities. It is apparent that some experts on quantum chemistry will be able to express their opinions with respect to the crystallization and the evaluation of the coefficients of supersaturation, since there has been some progress made in the field of quantum chemistry, such as: calculating a crystal lattice energy based upon experimental data according to Born-Haber's cycle, etc.

Considering that the potential energy between the two nearest particles is a simple function of distance, it is reasonable to determine the supersaturation coefficients or a degree of supersaturation for impure sugar solutions according to the same formula as that used for pure sugar solutions.

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Approved For Release 2009/04/15 : CIA-RDP80T00246A006800190002-5

1. Buckley, H.E., 1951. Crystal Growth, p.140, J-L, Moscow.

2. Genie, G.V., 1956. Etude et Construction d'un Appareil pour la mesure de la Sursaturation des solutions sucrees en ebullition. Sucr. belge, J-10:418.

3. McGinnis, R.A., 1951. Beet Sugar Technology, p. 298, Reinhold Publishing Co.,

4. Kuznetsov, V.D., 1953. Crystals and crystallization, p. 148, State Edition, Moscow.

5. Havens, E., 1953. La cristallisation du Sucre, p.39, Commission Internationale Technique de Sucrerie.

Approved For Release 2009/04/15 : CIA-RDP80T00246A006800190002-5